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<p>(21) International Application Number: PCT/GB88/00546</p> <p>(22) International Filing Date: 8 July 1988 (08.07.88)</p> <p>(31) Priority Application Number: 8716305</p> <p>(32) Priority Date: 10 July 1987 (10.07.87)</p> <p>(33) Priority Country: GB</p> <p>(71) Applicant (<i>for all designated States except US</i>): RAY-CHEM LIMITED [GB/GB]; Rolls House, 7 Rolls Buildings, Fetter Lane, London EC4 1NH (GB).</p> <p>(72) Inventor; and</p> <p>(75) Inventor/Applicant (<i>for US only</i>) : PENNECK, Richard, John [GB/GB]; Treeve, Westway, Lechlade, Gloucestershire GL7 3AU (GB).</p> <p>(74) Agents: DLUGOSZ, A., C.; Raychem Limited, Faraday Road, Dorcan, Swindon, Wiltshire SN3 5HH (GB) et al.</p>		<p>(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: ELECTRICAL WIRE</p> <p>(57) Abstract</p> <p>An electrical wire comprises an elongate electrical conductor, an inorganic arc-control layer surrounding the conductor, an insulating layer which surrounds the arc-control layer and comprises an aromatic polymer, and a secondary tracking control layer surrounding the insulating layer, the secondary tracking control layer having a comparative tracking index of at least 300V. The wire exhibits good electrical and mechanical properties characteristic of highly aromatic polymers together with good resistance to dry arcing and wet tracking.</p>			

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ELECTRICAL WIRE

This invention relates to electrical wires, and especially to wires that employ electrical insulation based on aromatic polymers.

Electrical wire and cable that use aromatic polymer insulation have been used for many years in numerous applications. For example wires that employ polyimide wraps or tapes usually bonded with fluoro-polymer adhesive layers have been used extensively as aircraft wire, for both civil and military applications. Other examples of aromatic insulation that have been used for equipment wire or "hook-up" wire, air frame wire and in wire harnesses include aromatic polyether ketones, polyether ether ketones, modified polyphenylene oxide, and polyimide amides. Highly aromatic polymers have been used successfully in many applications because they have a range of desirable properties especially high strength and toughness, abrasion resistance, temperature resistance, dielectric strength and are often inherently highly flame-retarded.

The combination of these properties has enabled wire and cable fabricated from these polymers to be

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used in small lightweight constructions. Such constructions have been used increasingly in both military and civil applications due to the high density and complexity of modern electrical systems.

However, these highly aromatic polymers suffer from a major problem: they are particularly susceptible to tracking. Tracking is a phenomenon associated with the formation of permanent and progressive conducting paths on the surface of the material by the combined effects of an electrical field and external surface pollution. Once commenced, the carbonaceous conducting deposits often extend quickly in dendritic fashion to give a characteristic "tree" pattern until failure occurs across the surface. Electrical tracking can occur when a damaged energised bundle of wires become wet e.g. from electrolytes or condensation. This tracking may lead to flashover and arcing that causes additional wires in the bundle to become damaged. A catastrophic cascade failure can result from a fault to a single wire if adjacent wires that are at a different electrical potential are also susceptible to tracking or if the bundle is in contact with a grounded structure. Tracking can occur at low voltages e.g. 100V a.c. or less but becomes less likely as the voltage is reduced.

A related phenomenon, to which these polymers are also highly susceptible, is that of breakdown due to arcing. In this case a potential difference between two conductors, or between a conductor in which the insulation has been mechanically damaged, and ground, can result in the formation of an arc between the con-

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ductors or between the conductor and ground. The high temperature of the arc causes the polymer to degrade extremely rapidly and form an electrically conductive carbonaceous deposit which can extend rapidly, as with wet tracking, and lead to catastrophic failure in which many or all of the wires in a bundle are destroyed. Arcing can occur at very low voltages, for example 24V d.c. or lower, and since, unlike tracking, no electrolyte or moisture is involved, it is a particularly hazardous phenomenon. Arcs may also be struck by drawing apart two conductors between which a current is passing as described for example by J.M. Somerville "The Electric Arc", Methuen 1959.

Another phenomenon that can be associated with tracking and arcing is erosion. In this case insulating material is removed by a vaporization process originated by an electrical discharge without the formation of electrically conductive deposits so that failure of the insulation will not occur until complete puncture of the insulation occurs.

According to the present invention, there is provided an electrical wire which comprises an elongate electrical conductor, an inorganic arc-control layer surrounding the conductor, an insulating layer which surrounds the arc-control layer and comprises an aromatic polymer and a secondary tracking control layer surrounding the insulating layer, the secondary tracking control layer having a comparative tracking index of at least 300V. The "comparative tracking index" (C.T.I.) of a polymer is defined below.

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By forming a wire in accordance with this invention it is possible to utilise the very good thermal, mechanical and electrical properties of aromatic polymers without the wire exhibiting a high propensity to track which is associated with highly aromatic polymers.

The aromatic polymer will normally have a carbonaceous char residue of at least 25%, preferably at least 30%, some polymers having a char residue of at least 40% and even at least 50%. This does not mean to say that a high char value is desired for its own sake, but simply that good mechanical and physical properties of these aromatic polymers including temperature stability and fire retardancy, are usually associated with high char residues.

The char residue of the polymer components in the electrical wire according to the invention can be measured by the method known as thermogravimetric analysis, or TGA, in which a sample of the polymer is heated in nitrogen or other inert atmosphere at a defined rate, e.g. 10°C per minute to a defined temperature and the residual weight, which is composed of char, is recorded. The char residue is simply the quantity of this residual char expressed as a percentage of the initial polymer after having taken into account any non polymeric volatile or non-volatile components. The char residue values quoted herein are defined as having been measured at 850°C and at a heating rate of 10°C per minute.

The preferred aromatic polymers which are used in this invention are well known to those skilled in the

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art, and reference may be made for example to U.S. Patents Nos. 3,025,605, 3,306,874, 3,257,357, 3,354,129, 3,441,538, 3,442,538, 3,446,654, 3,658,938, 3,677,921, 3,838,097, 3,847,867, 3,953,400, 3,956,240, 4,107,147, 4,108,837, 4,111,908, 4,175,175, 4,293,670, 4,320,224, and 3,446,654, British Patents Nos. 971,227, 1,369,210 and 1,599,106 and European Patent Applications Nos. 170,065, 124,276 and 178,185. Such polymers include polyketones, polyether ketones, polyether ether ketones, polyether sulphones, polyether ketone/sulphone copolymers, polyether imides and polyphenylene oxides. Blends of different polymers can be used. The polymers may be wholly aromatic or they may include one or more aliphatic moieties which may comprise pendant alkyl groups or may comprise alkylene groups in the polymer backbone. Preferably the or each aliphatic moiety has not more than 4, and more preferably not more than 3 carbon atoms. In the case of pendant alkyl groups, each group is most preferably a methyl group, while in the case of alkylene groups each group preferably has not more than 3 carbon atoms, and especially only one carbon atom, in the chain backbone, for example a methylene or isopropylidene group.

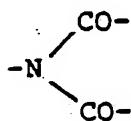
Preferred aromatic polymers are polymers with a melting or softening point of at least 250°C, particularly at least 300°C and which may be crystalline or amorphous. Softening points of amorphous polymers may conveniently be measured by thermomechanical analysis (TMA), in which case the softening point refers to the temperature at which the probe has reached 60% penetration. In one class of such polymers the polymer comprises, and preferably consists essentially of, units of the formula

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-Ar-Q-

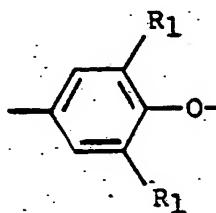
the units being the same or different,

wherein Ar represents an unsubstituted or substituted divalent aromatic radical and Q represents -O-, -S-, -SO₂-, -CO-, -NH-CO- or -COO-, or Ar represents a polyvalent radical and Q represents



each bond of the Q radical preferably being bonded directly to an aromatic carbon atom.

One preferred class of polymer comprises the polyphenylene oxides of the repeating unit



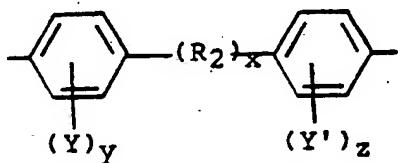
in which the groups R₁, which may be the same or different, each represents a hydrogen or halogen atom or a hydrocarbon atom having no tertiary alpha carbon atom.

In another class of aromatic polymers the aromatic polymer is a crystalline polyarylene ether comprising recurring units of the formula

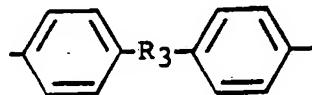
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-O-E-O-E'-

where E is the residue of a dihydric phenol and E' is the residue of an aromatic compound having an electron withdrawing group in at least one of the positions ortho and para to the valence bonds, the E and E' radicals being linked to the -O- radicals through aromatic carbon atoms. In one preferred sub-class, E is a radical of the formula

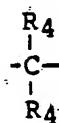


wherein R₂ is a divalent radical; x is 0 or 1; Y is a radical selected from halogen atoms, alkyl radicals containing 1 to 4 carbon atoms and alkoxy radicals containing 1 to 4 carbon atoms; y is 0, 1, 2, 3 or 4; Y' is a radical selected from halogen atoms, alkyl radicals containing 1 to 4 carbon atoms and alkoxy radicals containing 1 to 4 carbon atoms; z is 0, 1, 2, 3 or 4, and E' is a radical of the formula



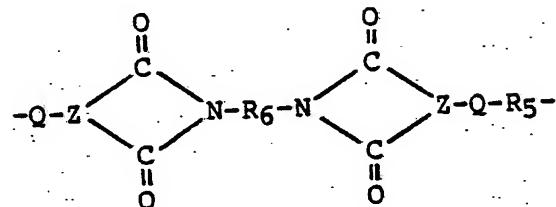
wherein R₃ is a sulphone, carbonyl, vinyl, sulphoxide, azo, saturated fluorocarbon, organic phosphine oxide or ethyldene radical. In this class preferred polysulphones are those in which y and z are 0, x is 1, R₃ is a sulphone radical and R₂ is a radical of the formula

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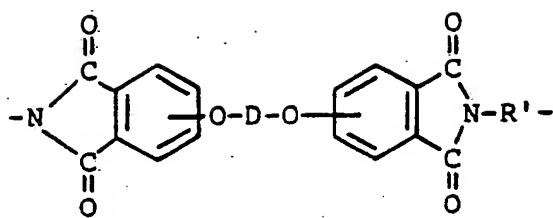
wherein each of R_4 is independently selected from the group consisting of hydrogen; alkyl radicals containing 1 to 4 carbon atoms; halogen-substituted alkyl radical containing 1 to 4 carbon atoms; aryl, alkaryl and aralkyl radicals containing 6 to 10 carbon atoms; and halogen-substituted aryl alkaryl and aralkyl radicals containing 6 to 10 carbon atoms.

In another class of aromatic polymers, the polymer is a polyether imide or polysulphone imide which comprises recurring units of the formula

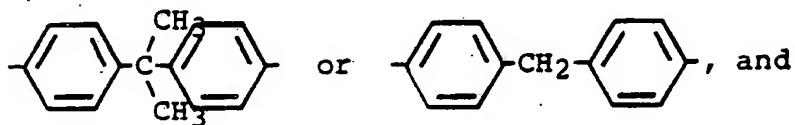


where Q is $-O-$ or $-SO_2-$, Z is a trivalent aromatic radical, R_5 is a divalent aromatic radical and R_6 is a divalent organic radical. Preferably the aromatic polymer has the general repeat unit

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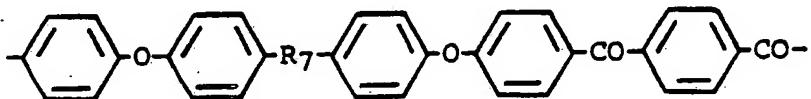


in which D represents a group of the formula:



R' represents an arylene group.

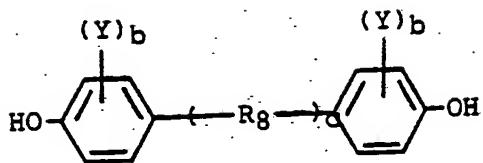
Another class of polymers is the polyetherketones that have repeating groups comprising aromatic ether and aromatic ketone groups together with an imide, amide, ester, benzoxazole or benzothiazole group. Examples of such polymers are those having repeating units of the formula:



where R7 represents an imide, amide or ester group.

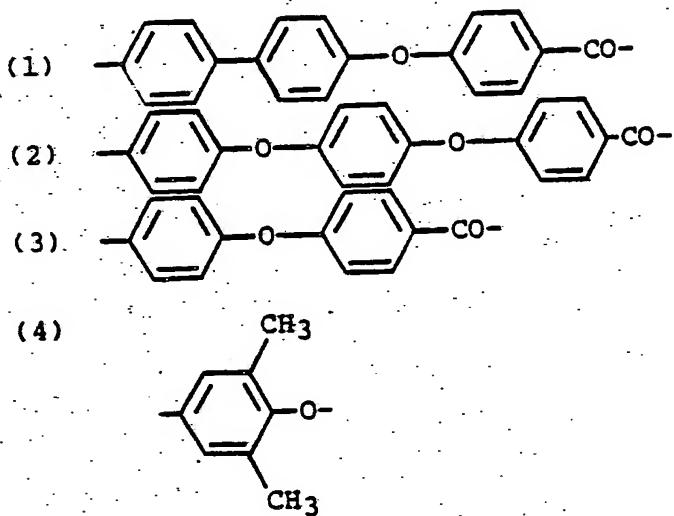
Yet another class of aromatic polymer is the polyarylates. Polyarylates that may be used include those that are derived from dihydric phenols and at least one aromatic dicarboxylic acid. Examples of such polymers include those derived from a dihydric phenol of the general formula

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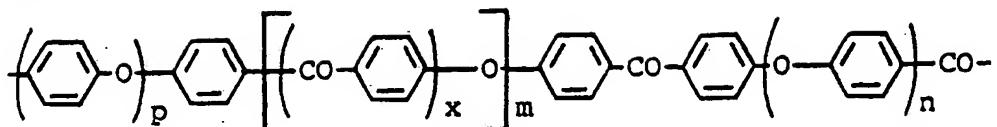
in which the groups Y, which may be the same or different, each represent a hydrogen atom, a C₁ to C₄ alkyl group, or a chlorine or bromine atom; b is 0 or an integer from 1 to 4; R₈ represents a divalent saturated or unsaturated hydrocarbon group, e.g. an alkylene, alkylidene, cycloalkylene or cycloalkylidene group, an oxygen or sulphur atom or a carbonyl or sulphonyl group; and c is 0 or 1.

Preferred aromatic polymers consist essentially of repeating units having one of the following formulae

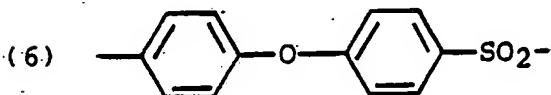
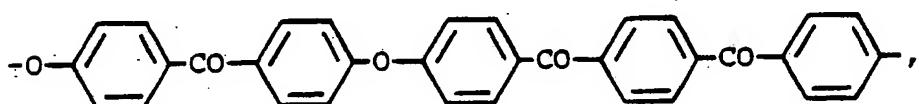
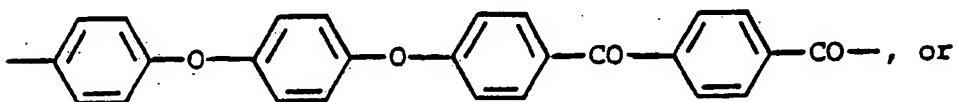


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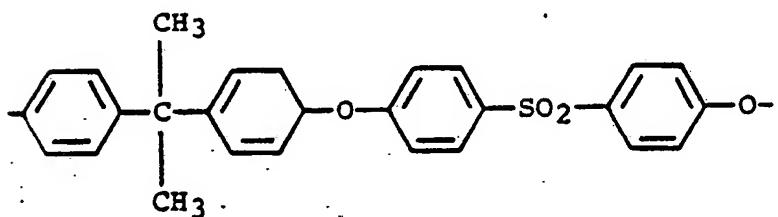
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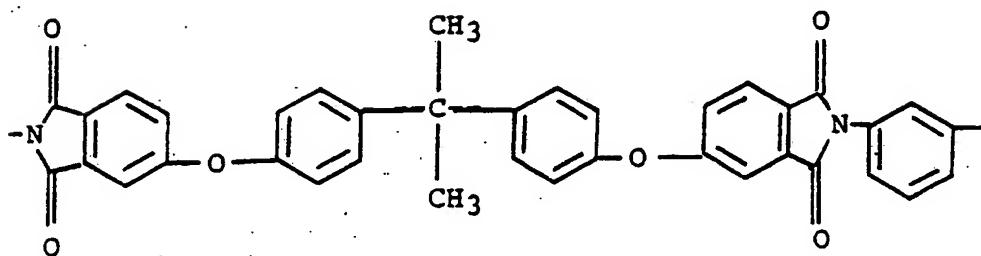
wherein each of x, m and n is 0 or 1, with n being 0 when x is 1, p is an integer from 1 to 4, with m being 1 and x being 0 when p is greater than 1, e.g.,



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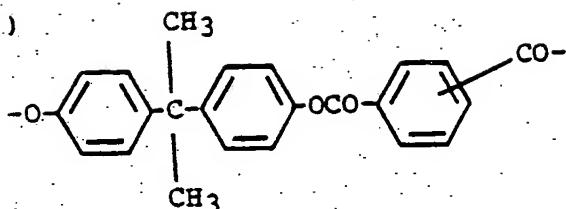


(8)



or

(9)



in which units derived wholly from isophthalic acid or terephthalic acid or a mixture of both are present.

Other polymers having aromatic moieties e.g. poly 1,12-dodecamethylene pyromellitimide or 1,13-tridecamethylene pyromellitimide, as described in U.S. patent No. 3,551,200, may be used.

Blends of any two or more of the above polymers may be employed as may copolymers based on any two or more of these polymers.

The preferred aromatic polymers will usually have a molar C:H ratio of at least 1.0, preferably at least 1.2, more preferably at least 1.3 and especially at least 1.4. The toughest polymers such as the polyaryl ether ketones, which are associated with high char residues, will have C:H ratios greater than 1.5.

The insulating layer may, in some cases, have an inner surface that has a C.T.I. of at least 250V. Preferably the C.T.I. of the inner surface of the principal insulating layer is at least 300V and most especially at least 500V. Such values for the C.T.I. will normally be associated with carbonaceous char levels of

not more than 10% by weight preferably not more than 5% by weight more preferably not more than 2% and especially 0%. The C.T.I. of the inner surface of the insulating layer may be achieved in certain cases by selection of the appropriate aromatic polymer. Alternatively it may be appropriate to blend the aromatic polymer with an aliphatic polymer in order to reduce the char level or increase the C.T.I. of the layer. We have found that the incorporation of an aliphatic polymer in the aromatic polymer can lead to a disproportionate reduction in the char residue of the blend, as described in our co-pending British patent application entitled "Electrical Wire and Cable" filed on even date herewith (Agent's ref: RK336), the disclosure of which is incorporated herein by reference. The preferred aliphatic polymers that may be blended with the aromatic polymer are the same as those referred to below for use as the secondary tracking control layer.

Alternatively or in addition, the insulating layer may be in the form of two or more layers, the outermost layer comprising the aromatic polymer, either alone or as a blend with one or more other polymers, and the inner layer comprising a polymer having a low char residue, e.g. not more than 10% by weight. The inner layer may, and preferably does, comprise one or more of the aliphatic polymers mentioned below.

The total thickness of the insulating layer will usually be in the range of from 50 to 250 micrometres, and especially from 75 to 200 micrometres. When it is in the form of more than one layer, the inner layer will normally have a thickness of from 75 to 125 micro-

metres, and the outer layer will normally have a thickness of up to 150 micrometres, preferably up to 100 micrometres, and especially up to 75 micrometres.

The purpose of the arc-control layer is to control the growth of the arc roots which, according to the invention, is achieved by controlling the arc diameter through the provision of a refractory, preferably adherent, layer on the electrical conductor, which will aid quick conductor melting and severance before more extensive wire or bundle damage can occur. Thus, for example, a layer of alumina, silica, silicon nitride, aluminium nitride, magnesium oxide, and titanium dioxide may be applied by any appropriate means, for example a vapour deposition method. Examples of such methods includes sputtering, chemical vapour deposition, flame spraying, plasma ashing, reactive ion plating, electron beam evaporation or by other techniques. Examples of refractory coatings and methods of forming them on a conductor are described in our patent application No. GB-2,144,260A (US 818,854), the disclosure of which is incorporated herein by reference. Alternatively a weathered mica coating may be employed, for example as described in our copending European applications filed on even date herewith and claiming priority from British applications Nos. 8716303 and 8716309, the disclosures of which are also incorporated herein by reference.

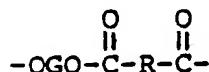
The thickness of the arc-control layer will depend on, amongst other things, the material from which it is formed. In the case of refractory layers, the thickness will normally be in the range of from 0.1 to

10 micrometres preferably 5 to 10 micrometres, and the layer will preferably adhere to the electrical conductor for example by provision of a metallic or refractory interlayer. For other materials, thicknesses up to 100 micrometres may be used.

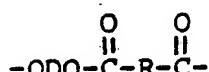
As stated above, the secondary tracking control layer has a C.T.I. of at least 300V. Preferably it has a C.T.I. of at least 400V, more preferably at least 500V and especially at least 600V. This normally will mean that the material from which the secondary tracking control layer is formed will have a carbonaceous char residue of not more than 10%, more preferably not more than 5%, most preferably not more than 2% and especially 0% by weight. The secondary tracking control layer preferably comprises an aliphatic polymer or blend of aliphatic polymers, although it is possible for the aliphatic polymer to include one or more aromatic moieties in addition to its aliphatic moieties, and indeed a number of preferred polymers do so. However the polymer should have sufficient aliphatic nature that its molar C:H ratio is not more than 1. Examples of aliphatic polymers and polymers containing aliphatic moieties (which will be referred to herein simply as aliphatic polymers for the sake of brevity) include olefin homopolymers and copolymers of olefins with other olefins and with other monomers e.g. vinyl esters, alkyl acrylates and alkyl alkacrylates, e.g. low, medium and high density polyethylene, linear low density polyethylene and ethylene alpha-olefin copolymers, ethylene/propylene rubber, butyl rubber, ethylene vinyl acetate, ethylene ethyl acrylate and ethylene acrylic acid copolymers, and linear or radial styrene

diene di- or tri-block copolymers e.g. styrene/butadiene, styrene/isoprene copolymers, styrene/butadiene/-styrene and styrene/isoprene/styrene, and hydrogenated versions of these block copolymers especially styrene/ethylene/ethylene/styrene block copolymers. A particularly preferred class of low charring polymers is the polyamides. Preferred polyamides include the nylons e.g. nylon 46, nylon 6, nylon 7, nylon 66, nylon 610, nylon 611, nylon 612, nylon 11, nylon 12, nylon 1212, and aliphatic/aromatic polyamides, polyamides based on the condensation of terephthalic acid with trimethylhexamethylene diamine (preferably containing a mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diamine isomers), polyamides formed from the condensation of one or more bisaminomethylnorbornane isomers with one or more aliphatic, cycloaliphatic or aromatic dicarboxylic acids e.g. terephthalic acid and optionally including one or more amino acid or lactam e.g. ϵ -caprolactam comonomers, polyamides based on units derived from laurinlactam, isophthalic acid and bis-(4-amino-3-methylcyclohexyl) methane, polyamides based on the condensation of 2,2-bis-(*p*-aminocyclohexyl) propane with adipic and azelaic acids, and polyamides based on the condensation of trans cyclohexane-1,4-dicarboxylic acid with the trimethylhexamethylene diamine isomers mentioned above. Other aliphatic polymers that may be used include polyesters e.g. polyalkylene terephthalate and especially polytetramethylene terephthalate, and cycloaliphatic diol/terephthalic acid copolymers e.g. copolymers of terephthalate and isophthalate units with 1,4-cyclohexanedimethoxy units, polysulphides, polyethers e.g. polybutylene ether copolymers, and especially polyether

esters such as those having polytetramethylene ether and polytetramethylene terephthalate blocks; aliphatic ionomers e.g. those based on metal salts of ethylene (meth)acrylic acid copolymers or sulphonated olefins such as sulphonated EPDM, and the like. Preferred aliphatic polymers include the polyamides mentioned above, polyethylene, polybutylene terephthalate, ionomers based on metal salts of methacrylated polyethylene, acrylic elastomers e.g. those based on methyl, ethyl or n-butyl acrylate or alkoxy-substituted ethyl or n-butyl acrylate polymers containing a cure site monomer and optionally ethylene comonomer, and block copolymers having long chain ester units of the general formula:



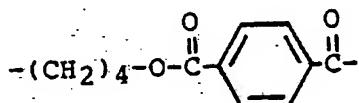
and short-chain ester units of the formula



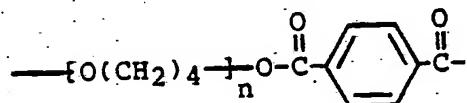
in which G is a divalent radical remaining after the removal of terminal hydroxyl groups from a polyalkylene oxide) glycol, preferably a poly (C₂ to C₄ alkylene oxide) having a molecular weight of about 600 to 6000; R is a divalent radical remaining after removal of carboxyl groups from at least one dicarboxylic acid having a molecular weight of less than about 300; and D is a divalent radical remaining after removal of hydroxyl groups from at least one diol having a molecular weight less than 250.

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Preferred copolymers are the polyether ester polymers derived from terephthalic acid, polytetramethylene ether glycol and 1,4-butane diol. These are random block copolymers having crystalline hard blocks with the repeating unit:

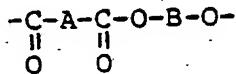


and amorphous, elastomeric polytetramethylene ether terephthalate soft blocks of repeating unit



having a molecular weight of about 600 to 3000, i.e. $n = 6$ to 40.

Other preferred aliphatic polymers include those based on polyether and polyamide blocks, especially the so called a "polyether-ester amide block copolymers" of repeating unit:



wherein A represents a polyamide sequence of average molecular weight in the range of from 300 to 15,000, preferably from 800 to 5000; and B represents a linear or branched polyoxyalkylene sequence of average molecular weight in the range of from 200 to 6000, preferably from 400 to 3000.

preferably the polyamide sequence is formed from alpha,omega-aminocarboxylic acids, lactams or diamine/-dicarboxylic acid combinations that include C₄ to C₁₄ alkylene carbon chains, and the polyoxyalkylene sequence is based on ethylene glycol, propylene glycol and/or tetramethylene glycol, and the polyoxyalkylene sequence constitutes from 5 to 85%, especially from 10 to 50% of the total block copolymer by weight. These polymers and their preparation are described in UK Patent Specifications Nos. 1,473,972, 1,532,930, 1,555,644, 2,005,283A and 2,011,450A.

The aliphatic polymer preferably has a C:H ratio of not more than 0.9, more preferably not more than 0.75, most preferably not more than 0.65 and especially not more than 0.55.

The aliphatic polymer may be unsubstituted or substituted. One class of aliphatic polymer that is particularly useful is the fluorinated polymers, preferably those containing at least 10%, more preferably at least 25% fluorine by weight. The fluorinated polymer may be a single fluorine containing polymer or a mixture of polymers one or more of which contains fluorine. The fluorinated polymers are usually homo- or copolymers of one or more fluorinated, often per-fluorinated, olefinically unsaturated monomers or copolymers of such a comonomer with a non-fluorinated olefin. The fluorinated polymer preferably has a melting point of at least 150°C, often at least 250°C and often up to 350°C, and a viscosity (before any crosslinking) of less than 10⁴ Pa.s at a temperature of not more than 60°C above its melting point. Preferred

fluorinated polymers are homo- or copolymers of tetrafluoroethylene, vinylidene fluoride or hexafluoropropylene, and especially ethylene/tetrafluoroethylene copolymers e.g. containing 35 to 60% ethylene, 35 to 60% tetrafluoroethylene by mole and up to 10% by mole of other comonomers, polyvinylidene fluoride, copolymers of vinylidene fluoride with hexafluoropropylene, tetrafluoroethylene and/or hexafluoroisobutylene, polyhexafluoropropylene, and copolymers of hexafluoropropylene and tetrafluoroethylene. Alternatively C₁-C₄ perfluoroalkoxy substituted perfluoroethylene homopolymers and copolymers with the above fluorinated polymers may be used.

The secondary tracking control layer may have a thickness of up to 100 micrometres, e.g. from 50 to 100 micrometres in the case of a polymeric layer. Thinner secondary tracking control layers may be provided by other means.

The polymeric insulation of the wire is preferably cross-linked. In general, however, the aromatic polymers will exhibit a lower degree of crosslinking than the aliphatic polymers, and in many cases the aliphatic polymers may be highly crosslinked while the aromatic polymers remain substantially uncrosslinked.

The polymeric composition may be cross-linked, for example, by exposure to high energy radiation.

Radiation cross-linking may be effected by exposure to high energy irradiation such as an electron beam or gamma-rays. Radiation dosages in the range 20

to 800 kGy, preferably 20 to 500 kGy, e.g. 20 to 200 kGy and particularly 40 to 120 kGy are in general appropriate depending on the characteristics of the polymer in question. For the purposes of promoting cross-linking during irradiation, preferably from 0.2 to 15 weight per cent of a prorad such as a polyfunctional vinyl or allyl compound, for example triallyl cyanurate, triallyl isocyanurate (TAIC), methylene bis acrylamide, metaphenylene diamine bis maleimide or other crosslinking agents, for example as described in U.S. patents Nos. 4,121,001 and 4,176,027, are incorporated into the composition prior to irradiation.

The polymers used for the various layers may include additional additives, for example reinforcing or non-reinforcing fillers, stabilisers such as ultra-violet stabilisers, antioxidants, acid acceptors and anti-hydrolysis stabilisers, pigments, processing aids such as plasticizers, halogenated or non-halogenated flame retardants, hydrated metal oxides such as alumina trihydrate and magnesium hydroxide, or decabromodiphenyl ether or combinations thereof, fungicides and the like.

The wires and cables according to the invention may be formed by conventional techniques. For example the polymers may be blended together if necessary in a mixer, together with any additional components, pelletised, and then extruded onto a wire conductor. Other non-preferred wires may be formed by a tape-wrapping method. For example a polyamide, e.g. trimethylhexamethylene terephthalamide may be dissolved in a solution of a polyamic acid and, after the solvent has been

evaporated, the aromatic polymer may be imidized by heat and cut into tapes which can then be wrapped around the conductor and underlying layers. However, it is preferred for the polymers to be melt-shapeable, so that the wire insulation can be formed by extrusion.

The wires may be used individually as equipment or "hook-up" wires, or airframe wires, or in bundles and harnesses, both jacketted and unjacketted, and may be used in multiconductor cables. The wires, harnesses or cables may be unscreened or they may be provided with a screen to protect them from electromagnetic interference, as well known in the art. In addition flat cables may be formed using the insulation materials according to the invention, either employing flat conductors or round conductors.

The invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is an isometric view of part of an electrical wire according to the invention;

Figure 2 is a schematic view of the test arrangement for wet tracking; and

Figure 3 is a schematic view of the test arrangement for dry arcing.

Referring initially to figure 1 of the accompanying drawings, an electrical wire comprises a conductor 11 which may be solid or stranded as shown and

is optionally tinned. A 10 micrometre thick silica or alumina layer 12 is formed on the conductor by a vacuum deposition process, e.g. by sputtering, 5 micrometre intermediate layer formed from for example aluminium optionally being provided in order to improve adhesion of the layer 12 to the conductor 11. A 100 to 200 micrometre thick aromatic polymer insulation 13 is then extruded onto the coated conductor followed by a 100 micrometre thick tracking control layer 14 formed e.g. from an ethylene-tetrafluoroethylene copolymer. After both layers have been extruded, the insulation is irradiated by high energy electrons, to a dose of about 120 kGy to crosslink the tracking control layer 14 and optionally also the aromatic polymer layer (depending on the aromatic layer).

The following Examples illustrate the invention. In the Examples the following test procedures were used:

WET TRACKING TEST

This test is designed to simulate the condition occurring when a damaged wire bundle comes into contact with an electrolyte. Under actual conditions, the electrolyte may be moisture containing dust particles or other ionic contaminant. Damage to the bundle may occur through a number of reasons e.g. abrasion, hydrolysis of the insulation, aging, etc. Current flow through the electrolyte results in heating and evaporation of the solution. This causes one or more dry bands to appear across which the test voltage is

dropped, resulting in small, often intense, scintillations which damage the insulation.

Figure 2 shows the sample set-up. A wire bundle 1 is prepared from seven 14cm lengths 2 of 22AWG tinned-copper or nickel-plated copper conductor coated with a layer of the wire insulation under test. The bundle 1 is arranged with six wires around one central wire and is held together using tie wraps 3 so that the wires are not twisted. Two adjacent wires are notched circumferentially to expose 0.5mm bare conductor on each wire. The notches 4 are arranged such that they are 5mm apart with the tie wraps 5mm either side of them. One end of each wire is stripped to enable connections to be made to the power supply via insulated crocodile clips. The sample is held at an angle of 30 degrees to the horizontal using a simple clamp made of an electrically insulating resin so that the damaged wires are uppermost and the stripped ends are at the upper end of the bundle. A piece of filter paper 5 20 x 10mm wide is wrapped around the bundle approximately 2mm above the upper notch; this is best held in place with the upper tie wrap.

A peristaltic pump conveys the electrolyte from the reservoir to the sample via a dropping pipette 6, and a power supply is provided to energise the bundle. The electrolyte used is 2% sodium chloride and 0.02% sodium dodecyl sulphate surfactant in distilled or deionised water. The pump is set to deliver this solution at a rate of approximately 60mg per minute through the pipette 6 which is positioned 10mm vertically above the filter paper 5.

The power is supplied by a 3-phase 400Hz 115/200V generator of at least 5kVA capacity or a single phase 50Hz 115V transformer of at least 3kVA capacity. A device for recording time to failure is provided which records the time when either a wire goes open circuit, or when a circuit breaker comes out. Leakage currents can be followed with the use of current clamps surrounding the wires and connected to a suitable oscilloscope.

In the case of the three phase supply, adjacent wires of the bundle are connected to alternate phases of the power supply via 7.5A aircraft type circuit breakers with the central wire connected directly to neutral. In the case of the single phase supply, alternate wires are connected to neutral with the remaining wires including the central conductor to live. A few drops of electrolyte are allowed to fall onto the filter paper to ensure saturation prior to starting the test. The power is switched on and the timer started as soon as a leakage current has been detected. The test is allowed to continue until:

- a) one or more circuit breakers come out;
- b) a wire becomes open circuit; or
- c) 8 hours have elapsed.

The condition of the final bundle and the time to failure is noted in all cases. Where failure has occurred due to breakers coming out, the power is then reapplied and each breaker is reclosed in turn until there is no further activity. The condition of the bundle is again noted.

Where a wire has gone open circuit, the power is reapplied and the test continued for a total of 8 hours. Wire insulations exhibiting "failures" due to (b) or (c) may be considered to be good non wet-tracking insulation if no more than two of the originally undamaged wires become open circuit.

Dry Arc Test

This test is designed to simulate what happens when a fault in a wire bundle causes arcing under dry conditions. A graphite rod is used to initiate the arc which causes thermal degradation of the insulation. Continuation of the fault current can only occur through the wire bundle under test due to shorting across adjacent phases through a conductive char, or direct conductor-conductor contact such as might occur if the insulation is totally removed by the duration of the arc.

Figure 3 shows the sample set-up. A wire bundle 21 is prepared from seven 10cm lengths 22 of 22AWG tinned-copper or nickel-plated copper conductor coated with a layer of the wire insulation under test. The bundle 22 is arranged with six wires around one central wire and held together with tie wraps spaced about 5cm apart. One of the outer wires is notched circumferentially between the tie wraps to expose 0.5mm bare conductor and one end of each wire is stripped to enable connections to be made via insulating crocodile clips.

A rod 23 is provided which is made of a spectrographically pure graphite, diameter 4.6mm, with

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an impurity level not more than 20ppm. It is prepared before each test by sharpening one end using a conventional pencil sharpener of European design to give an angle of 10 degrees off vertical with a tip diameter of 0.4 ± 0.1 mm. A 100g weight 24 is clamped onto the top of the rod 23 to maintain contact during the arc initiation and also acts as a device to limit the depth of penetration of the rod by restricting its downward travel. The rod passes through a PTFE bush which allows it to slide freely up and down.

The arrangement of levers enables precise positioning of the rod 23 on the wire bundle 21 which is held securely in place by means of a simple clamp 25 made of an electrically insulating resin and mounted on a block 26 made of the same material.

The power source can be either:

- a) a 3-phase 400Hz 115/200V generator of at least 5kVA capacity
- b) a single phase 50Hz 115V transformer, at least 3kVA capacity
- c) 24V d.c. supplied by two 12V accumulators.

The fault current is detected by means of current clamps surrounding the connecting leads and the voltage at failure is measured using a 10:1 voltage probe. The transducer signals are fed into a multi-channel digital storage oscilloscope where they can be displayed and manipulated to obtain power curves (voltage x current) and energy (integration of power curve).

The wire bundle 21 is positioned in the clamp 25 so that the notched wire is uppermost. Adjacent wires of the bundle are connected to different phases of the supply through 7.5A aircraft type circuit breakers, and the central wire is connected directly to neutral. In the case of single phase or d.c. supplies, alternate wires are connected to neutral or the negative terminal, with the remaining wires, including the central wire, connected through circuit breakers to live or the positive terminal. The carbon rod is also connected to neutral or the negative terminal and positioned so that the point is in contact with the exposed conductor. The gap between the 100g weight and the PTFE bush is adjusted to the diameter of the insulated wire under test, using a suitable spacer to limit the penetration of the rod into the sample. A voltage probe is connected across the damaged wire and the rod, and current clamps positioned on each of the three phases, or on the wires connected to the live side of the supply. A protective screen is placed in front of the test set-up and the power switched on. A material is deemed to pass this test if:

- a) no circuit breakers come out and the activity is relatively non-eventful, or
- b) there is no further activity on resetting the breakers after a non-eventful test.

In addition, non-tracking materials will have relatively few spikes in the current trace with a correspondingly low total energy consumed. Tracking materials, on the other hand, show many spikes usually on all three phases, which are accompanied by violent crepitation and large energy consumption.

CTI Test

This method is a modification of IEC 112 which measures the low voltage track resistance (up to 600V) as Comparative Tracking Index (CTI) of materials in the presence of an aqueous contaminant.

The samples of each polymeric layer are prepared by either compression or injection moulding plaques with minimum thickness of 3mm and with sufficient area to ensure that during the test no liquid flows over the edge of the sample. Before testing, the surface of the sample is cleaned with methanol to remove any surface contamination.

The test apparatus is as described in IEC 112. It consists of two platinum electrodes, each with one end chisel-shaped to an angle of 30 degrees. The electrodes are symmetrically arranged such that the opposing chisel faces are vertical and 4.0 ± 0.1 mm apart when placed on the surface of the specimen.

The power supply consists of a 0.5kVA transformer capable of supplying an a.c. voltage in the range 100-600V at 50Hz. A rheostat is incorporated into the circuit so that the short circuit current may be adjusted to give 1.0 ± 0.1 amp. An over-current relay is provided which shuts off the HV supply when a current of at least 0.5 amps flows for 2 seconds, the criteria for failure.

A device for dropping electrolyte solution between the electrodes is provided. This consists of a

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peristaltic pump which draws liquid from a reservoir and pumps it out of a needle situated at height of 30-40mm above and between the electrodes. The dropping rate is set to 1 drop every 30 ± 5 seconds with a drop volume of 20 ± 3 mm³. Before the test, the needle is cleaned and purged with several drops of electrolyte to ensure the correct concentration of reagent is used.

The electrolyte solution used in these tests is $0.1\pm 0.002\%$ ammonium chloride and 0.01% sodium dodecyl sulphate surfactant in deionised water and has a resistivity of 405 ± 5 ohm.cm at 23°C.

By using a surfactant, reproducible results have been obtained on homogeneous samples. However, the type of surfactant used can greatly affect the CTI values obtained. Sodium dodecyl sulphate was chosen as this gave a working range of below 150 (for known badly tracking materials) to above 600 for non-tracking materials.

Test Procedure

The specimen is put into position and the electrodes lowered on to the surface. A suitable voltage is chosen and the short circuit current adjusted accordingly. The electrolyte is then allowed to drop between the electrodes until either

- a) tracking occurs
- b) the sample erodes through to the supporting base
- c) at 600V, the sample withstands 50 drops.

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For those materials which track, the test is then repeated at at least three other voltages such that two voltages give results above 50 drops, and two give results below 50 drops. A curve of drops to failure versus applied voltage is plotted from which is read the voltage at which 50 drops would cause failure. This voltage is the comparative tracking index (CTI).

For those materials which withstand 50 drops at 600V, CTI is then quoted as >600 and the erosion of the sample is measured by preweighing a plaque of the material, running the test at 400V for 101 drops of electrolyte, and then reweighing the sample after removing any loose surface debris. The erosion is quoted as mg of material lost.

For those samples which penetrate through to the supporting base during the test, erosion is quoted as mg lost at 400V after 101 drops, or after complete penetration, stating the number of drops required for this to occur e.g. 75mg (80 drops).

The following wire constructions were prepared by use of a 20mm Baughan extruder for the polymeric layers and by sputtering for the inorganic layers. In the cases where a blend has been used, it has been prepared using a Baker Perkins twin screw extruder. The conductor was 22 AWG nickel plated copper unless otherwise stated. The results for the wet and dry tracking tests are shown in the table.

Example 1

A 10 μm silica arc control layer on top of a 5 μm aluminium interlayer was coated with 160 μm of polyaryletheretherketone as the primary insulation layer and 75 μm crosslinked ethylenetetrafluoroethylene as the secondary tracking control layer.

Example 2

A 6-7 μm alumina arc control layer on top of a 7 μm aluminium interlayer was coated with 125 μm of polyaryletheretherketone as the primary insulation layer and 125 μm of a blend of polytetramethylene terephthalate and a poly(ether-ester) block copolymer comprising approximately 57% by weight polybutylene terephthalate hard blocks and approximately 43% by weight poly(butylene glycol polyether terephthalate) soft blocks in the ratio of 70:30 as the secondary tracking control layer. (22 AWG copper conductor).

Example 3

A 6 μm silica arc control layer on top of a 5.7 μm aluminium interlayer was coated with 125 μm of polyaryletheretherketone as the primary insulation layer and 125 μm of a blend of polytetramethylene terephthalate and a poly(ether-ester) block copolymer comprising approximately 57% by weight polybutylene terephthalate hard blocks and approximately 43% by weight poly(butylene glycol polyether terephthalate) soft blocks in the ratio of 70:30 as the secondary tracking control layer.

Example 4 (Control)

A 6-7 μm silica arc control layer on top of a 7 μm aluminium interlayer was coated with 125 μm of polyaryletheretherketone as an insulating layer.

Example 5 (Control)

100 μm polyaryletheretherketone as the inner insulating layer with 100 μm of a blend of polytetramethylene terephthalate and a poly(ether-ester)block copolymer comprising approximately 57% by weight poly(tetramethylene terephthalate) hard blocks and approximately 43% by weight poly(tetramethylene glycol polyether terephthalate) soft blocks in the ratio of 70:30 as the outer insulating layer.

Example 6 (Control)

A 125 μm polyaryletheretherketone layer as the sole insulation.

TABLE

Tracking Test Results

Example	Arc Control Layer	Primary Insulation	Secondary Tracking Control Layer	(50Hz, 115V)	
				Wet	Dry
1	Silica	PEEK	Cross-linked ETFE	Pass	Pass
2	Alumina	PEEK	PBT/poly(ether-ester) block copolymer	Pass	Pass
3	Silica	PEEK	PBT/poly(ether-ester) block copolymer	Pass	Pass
4 (Control)	Silica	PEEK		Fail	Fail
5 (Control)	-	PEEK	PBT/poly(ether-ester) block copolymer	-	Fail
6 (Control)	-	PEEK	-	Fail	Fail

The CTI of each of the secondary tracking control layers of Examples 1 to 3 and 5 was greater than 600 V.

CLAIMS:

1. An electrical wire which comprises an elongate electrical conductor, an inorganic arc-control layer surrounding the conductor, an insulating layer which surrounds the arc-control layer and comprises an aromatic polymer, and a secondary tracking control layer surrounding the insulating layer, the secondary tracking control layer having a comparative tracking index of at least 300V.
2. A wire as claimed in claim 1, wherein the arc-control layer has a char residue of not more than 2% by weight.
3. A wire as claimed in claim 2, wherein the arc-control layer has a char residue of not more than 0% by weight.
4. A wire as claimed in any one of claims 1 to 3, wherein the arc-control layer has a thickness in the range of from 0.1 to 10 micrometres.
5. A wire as claimed in claim 4, wherein the inorganic material has been deposited by a vacuum deposition process.
6. A wire as claimed in claim 4 or claim 5, wherein the inorganic material comprises an oxide, nitride or oxynitride of aluminium, silicon, or titanium.
7. A wire as claimed in any one of claims 1 to 6, wherein the aromatic polymer comprises a polyaryl ether

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ketone, a polyaryl ether sulphone, a polyarylether, a polyarylate and/or a polyether imide.

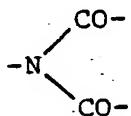
8. A wire as claimed in claim 7, wherein the aromatic polymer comprises:

i) units of the general formula:

-Ar-Q-

the units being the same or different,

wherein Ar represents an unsubstituted or substituted divalent aromatic radical and Q represents -O-, -S-, -SO₂-, -CO-, -NH-CO- or -COO-, or Ar represents a polyvalent radical and Q represents



the Q radical preferably being bonded directly to an aromatic carbon atoms;

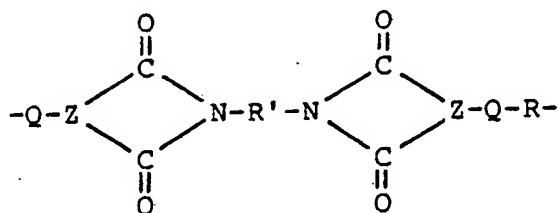
ii) a crystalline polyarylene ether comprising recurring units of the formula:

-O-E-O-E'-

wherein E is the residue of a dihydric phenol and E' is the residue of an aromatic compound having an electron withdrawing group in at least one of the positions ortho and para to the valence bonds, the E and E' radi-

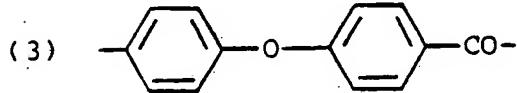
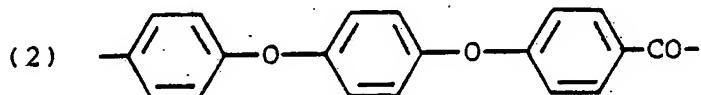
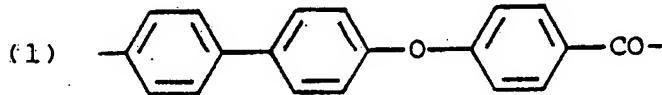
cals being linked to the -O- radicals through aromatic carbon atoms; or

iii) polyether imide or polysulphone imide which comprises recurring units of the formula

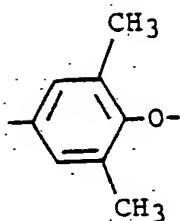


where Q is -O- or -SO₂, z is a trivalent aromatic radical, R is a divalent aromatic radical and R' is a divalent organic radical.

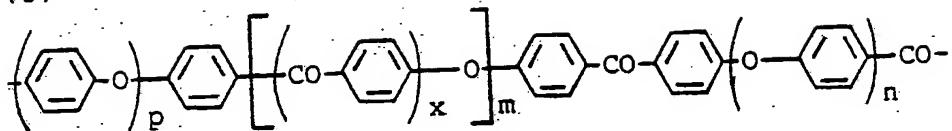
9. A wire as claimed in claim 8, wherein the aromatic polymer comprises a polymer having a repeating unit of the formula:



(4)

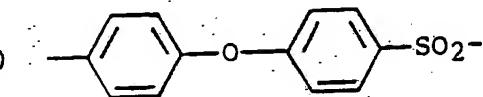


(5)

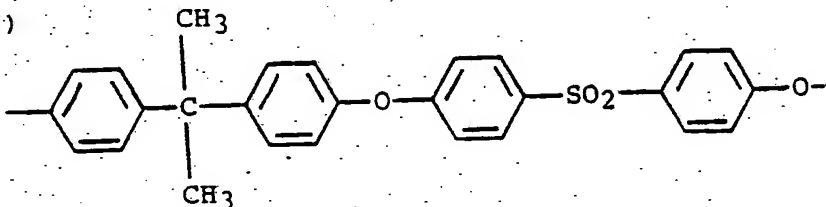


wherein each of x, m and n is 0 or 1, with n being 0 when x is 1, p is an integer from 1 to 4, with m being 1 and x being 0 when p is greater than 1,

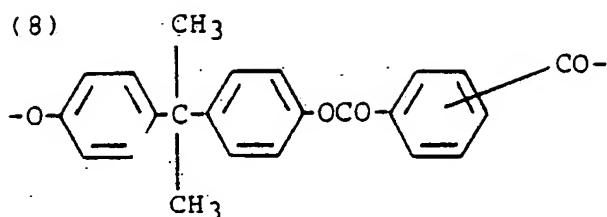
(6)



(7)

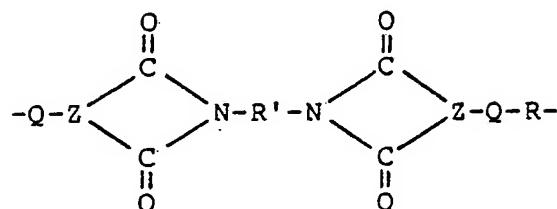


(8)



in which the units may be derived wholly from terephthalate acid or isophthalic acid or both;

(9)



10. A wire as claimed in any one of claims 1 to 9, wherein the aromatic polymer is blended with one or more aliphatic polymers.

11. A wire as claimed in any one of claims 1 to 10, wherein the insulating layer is in the form of a plurality of layers, at least the outermost layer comprising the aromatic polymer, and at least the inner layer comprising a polymer having a carbonaceous char residue of not more than 10% by weight.

12. A wire as claimed in claim 11, wherein the inner layer of the insulating layer comprises an aliphatic polymer.

13. A wire as claimed in any one of claims 10 to 12, wherein the or each aliphatic polymer of the insulating

layer comprises a polyolefin; a copolymer of an olefin with an olefin, an alkyl acetate, an alkyl acrylate, a vinyl ester; a polyamide; a polyether; a polyester, an ionomer or an acrylic polymer.

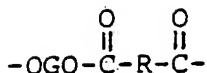
14. A wire as claimed in any one of claims 1 to 13, wherein the secondary tracking control layer has a comparative tracking index of at least 400 preferably 500.

15. A wire as claimed in any one of claims 1 to 14, wherein the secondary tracking control layer has a char residue of not more than 5%.

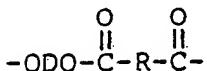
16. A wire as claimed in any one of claims 1 to 15, wherein the secondary tracking control layer comprises an aliphatic polymer.

17. A wire as claimed in claim 16, wherein the aliphatic polymer of the secondary tracking control layer is a polyolefin, a copolymer of an olefin with an olefin, an alkyl acetate, an alkyl acrylate or a vinyl ester, a polyamide, a polyester, an ionomer or an acrylic rubber.

18. A wire as claimed in claim 17, wherein the aliphatic polymer of the secondary tracking control layer comprises polyethylene, a crystalline polyamide, an amorphous aromatic/aliphatic polyamide, an ionomer based on a metal salt of methacrylated polyethylene, polybutylene terephthalate, a styrene/diene di- or tri-block copolymer or hydrogenated version thereof or a block copolymer having long-chain ester units of the general formula:



and short-chain ester units of the formula



in which G is a divalent radical remaining after the removal of terminal hydroxyl groups from a polyalkylene oxide) glycol, preferably a poly (C₂ to C₄ alkylene oxide) having a molecular weight of about 600 to 6000; R is a divalent radical remaining after removal of carboxyl groups from at least one dicarboxylic acid having a molecular weight of less than about 300; and D is a divalent radical remaining after removal of hydroxyl groups from at least one diol having a molecular weight less than 250.

19. A wire as claimed in claim 16, wherein the aliphatic polymer of the secondary tracking control layer is a fluorinated polymer.

20. A wire as claimed in claim 19, wherein the aliphatic polymer of the secondary tracking control layer is a homopolymer or copolymer of vinylidene fluoride polymer, a hexafluoropropylene, polytetrafluoroethylene or a C₁-C₅ perfluoroalkoxy substituted perfluoroethylene.

21. A wire as claimed in any one of claims 1 to 19, wherein the secondary tracking control layer is cross-linked.

Fig.1.

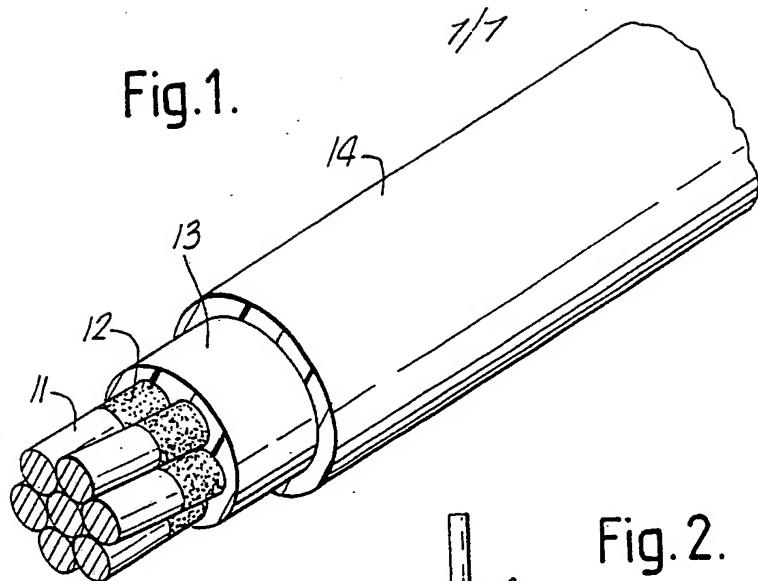


Fig. 2.

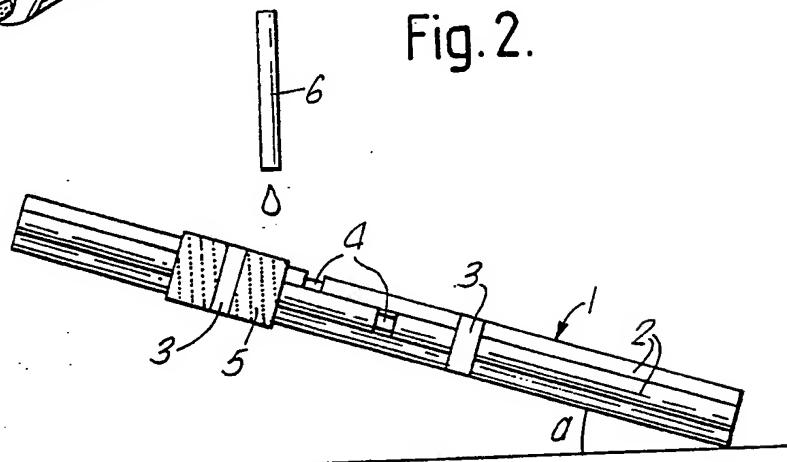
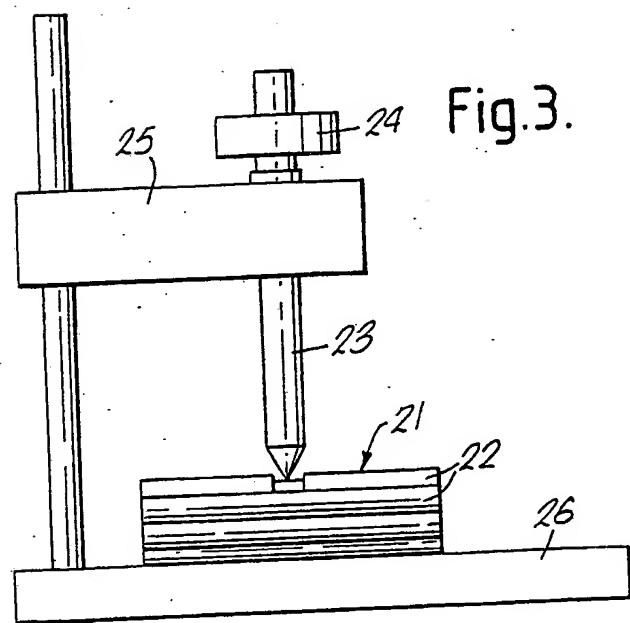


Fig. 3.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 88/00546

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁴: H 01 B 7/02; H 01 B 3/10; H 01 B 3/42; H 01 B 3/44

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
IPC⁴	H 01 B

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT*

Category ⁸	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A, 0188370 (RAYCHEM LTD) 23 July 1986, see claims 1,3,5,6,13,15; page 10, lines 4-27; page 11, paragraph 2	1,4,6,7,11- 13,16-21
Y	--	1,4,6-9,11- 13,16-21
X	EP, A, 0132343 (RAYCHEM LTD) 30 January 1985, see claims 1,10,14,15,16,19; page 13, line 33 - page 15, line 12; page 38, lines 15-21 & GB, A, 2144260 (RAYCHEM LTD) 27 February 1985 (cited in the application)	1,4-13,16-21
A	EP, A, 0157466 (IMPERIAL CHEMICAL IND. PLC) 9 October 1985 see claims 1,7; page 2, line 35 - page 3, line 19	1,7,8,9
Y	EP, A, 0103487 (RAYCHEM CORP.) 21 March 1984, see claims 1-3,5-9	1,4,6-9, 11-13,16-21
<hr/>		

* Special categories of cited documents: ¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search
4th October 1988

Date of Mailing of this International Search Report

31.10.88

International Searching Authority

Signature of Authorized Officer

EUROPEAN PATENT OFFICE

P.C.G. VAN DER PUTTEN

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. GB 8800546
SA 23149

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
 The members are as contained in the European Patent Office EDP file on 19/10/88
 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A- 0188370	23-07-86	JP-A-	61165910	26-07-86
EP-A- 0132343	30-01-85	WO-A-	8500462	31-01-85
		GB-A, B	2144260	27-02-85
		AU-A-	3151584	07-02-85
		GB-A, B	2182800	20-05-87
		GB-A, B	2183079	28-05-87
		GB-A, B	2183080	28-05-87
		EP-A-	0249252	16-12-87
		CA-A-	1236537	10-05-88
EP-A- 0157466	09-10-85	JP-A-	60238357	27-11-85
		US-A-	4654263	31-03-87
EP-A- 0103487	21-03-84	GB-A, B	2127210	04-04-84
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		US-A-	4521485	04-06-85
		CA-A-	1214528	25-11-86
		US-A-	4678709	07-07-87